# Spectra of collisional complexes containing a hydrogen or an alkali metal atom, considered in the approximation of a short-radius potential

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The approximation of a zero-radius potential is used to develop a theory of spectra representing the absorption of light in the course of collisions of a hydrogen atom in the ground state with a particle Y characterized by a single parameter, which is its electron scattering length. An analytic expression is obtained for the normalization integral of the Coulomb Green function and this expression is used to obtain a formula for the wave functions normalized to unity, the dipole moments of a transition from the ground state, and the absorption coefficients of light as functions of the transition energy. The absorption spectra are calculated for a number of values of the scattering length and their dependence on this length is analyzed. The method of a modified orbital quantum number is used to show that the theory can be generalized to the case of replacement of a hydrogen atom with a many-electron atom which has just one outer electron.

## 1. INTRODUCTION

The subject of collisions of atoms and molecules in an optical field has begun to develop as an independent topic from the early seventies.[1–8] This approach is of interest from the point of view of stimulation of collision processes (for example, those used in pumping of lasers[9]) and for reconstruction of the potentials of the interaction between colliding particles (see, for example, Refs. 10–12). However, if the offset from an atomic absorption line is sufficiently large, the dipole moment of the transition may change considerably and the problem of reconstruction of the potential from the absorption spectrum of a collisional $X + Y$ complex becomes much more difficult to tackle.

Studies of the absorption spectra of a $X + Y$ system were reported in Refs. 13–20: in accordance with the assumptions made, the decisive stage of the process is the phototransfer of an electron $X + Y + \hbar\omega \rightarrow X^+ + Y^-$; X is a rare-gas atom and Y is a halogen atom in Refs. 13–17. The profile of the corresponding absorption band is very wide and is frequently greater than a typical energy separation between the terms of an atom. The dipole moment of a transition obviously cannot be regarded as constant over such large energy intervals, and it cannot be even approximated by some simple function. The method of a potential with a short radius of action was used in studies of such processes in Refs. 19–21. Our preliminary calculations carried out in accordance with the theory of Ref. 20 demonstrated that the results were in agreement with the experiments[14–16] in those cases when one would expect the ion model to be correct. However, it is clear that this ion approximation is not always applicable and in any case it breaks down near atomic levels.

The purpose of the present investigation was to develop a theory of the spectra representing the processes described above using a zero-radius potential without invoking any additional assumptions in the electron part of the problem and in particular without recourse to the assumption that there is a transition to an ionic state. The problem formulated in this way had not been solved before even in the simplest model case of a collision between a hydrogen atom in its ground state and a particle Y whose potential for the interaction with an electron can be modeled by a $\delta$ potential.

## 2. THEORY

As usual, the problem of a phototransition in a molecular system can be divided into two parts: 1) the electron part, which when solved gives the electron terms, the electron wave functions, and the dipole moments of a transition as a function of the distance between colliding particles; 2) the nuclear part of the problem, the solution of which makes it possible to calculate the absorption spectrum on the assumption that the terms and dipole moments of the transitions are known.

The nuclear part of the problem will be solved in a traditional manner. We shall describe the absorption spectrum of a collisional complex by a reduced absorption coefficient $q$. It is related to the optical density $D$ by

$$q = \frac{D \ln 10}{l[\mathrm{H}][\mathrm{Y}]},$$

where $l$ is the optical path. In the case of a weak field the Landau–Zener expression gives[1]

$$q = \frac{16\pi^3\omega}{3c}\sum_{\omega}\frac{R_\omega^2}{\Delta F(R_\omega)}|d_{if}(R_\omega)|^2\left\langle 1 - \frac{U_i(R_\omega)}{E_v}\right\rangle^{1/2}, \qquad (1)$$

where $\omega$ is the angular frequency of an electromagnetic field (in atomic units this frequency is equal to the photon energy, because $\hbar = 1$ a.u.); $c$ is the velocity of light; $R_\omega$ is the distance between the colliding particles; $\Delta F_\omega$ is the relative slope of the terms; $d_{if}$ is the dipole moment of the investigated transition. The summation in Eq. (1) extends to all the points $R_\omega$ along the axis joining the colliding particles and equal to $R$, where the relationship $U_f(R_\omega) - U_i(R_\omega) = \omega$ is obeyed; $U_i$ and $U_f$ are the terms representing the ground (initial) and excited (final) states of the molecular system. The ground state, raised by $\omega$, crosses terms of the excited states at these points; $E_v$ is the relative kinetic energy of a collision at infinity. The angular brackets denote averaging over the velocities.

We shall now consider the electron part of the problem. The absorption of a photon occurs when the distance between colliding particles is large: $R \gg 1$ a.u. In this case the interaction between a hydrogen atom in its ground state and

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a perturbing Y particle can be ignored because the electron wave function for the ground state is identical with the wave function of the hydrogen atom:

$$\Psi_i=2\exp(-r)Y_{00}, \tag{2}$$

where **r** is the radius vector of an electron and $Y_{lm}$ is a spherical function. In this approximation the ground-state term ($U_i = 0.5$) is independent of $R$. In calculation of the absorption spectrum on the basis of Eq. (1) we have to proceed in steps of $\Delta R$ along a certain interval of the variable $R$ and at each point we have to find the following: 1) the term of the excited state $U_f(R)$ and the photon energy $\omega = U_f(R_\omega) + 0.5$; 2) the wave function $\Psi_f$ of the excited state and the dipole moment of the transition $d_{if}(R\omega)$; 3) the relative slope of the terms $\Delta F(R_\omega)$, which in this case is identical with the modulus of the slope of the excited-state term

$$\Delta F(R_\omega)=\left|\frac{dU_f(R_\omega)}{dR_\omega}\right|.$$

The tasks are listed under 1)–3) and represent the electron part of the problem.

Using a zero-radius potential, we can describe the interaction of an electron with a neutral particle by analogy with the theory of low-energy scattering postulating that the characteristic length of the potential of the interaction between the electron and the neutral particle is small compared with the electron wavelength near the Y center. The idea behind this method is similar to that introduced by Fermi in Ref. 22. Following this idea, the potential of the interaction between an electron and a neutral particle is replaced with the $\delta$ potential. The only parameter characterizing the individual nature of the particle Y is the scattering length $a_0$ of the electron colliding with this particle. The problem therefore reduces to an investigation of the motion of an electron in the field of the Coulomb and $\delta$ potentials, whose centers are separated by a distance $R$.

The terms obtained in the zero-phase potential approximation have been analyzed on many previous occasions (see, for example, Refs. 23–28). They are found by matching the wave functions near a point where the $\delta$ potential is located ($\mathbf{r} = \mathbf{R}$). This condition leads to a transcendental equation for the terms[29]

$$\Phi(n, R)=-a_0^{-1}, \tag{3}$$

$$\Phi(n,R)\equiv\frac{2\Gamma(1-n)}{n}\left\{\left(\frac{n^2}{2R}-\frac{1}{4}\right)W_{n,1/2}(2\gamma R)M_{n,1/2}(2\gamma R)\right.$$
$$\left.+W'_{n,1/2}(2\gamma R)M'_{n,1/2}(2\gamma R)\right\}.$$

The following notation is used in Eq. (3): $n = (-2E)^{-1/2}$, where $E$ is the energy of an electron $E(R) = U_f(R)$; $\Gamma$ is the gamma function; $M_{n,1/2}$ and $W_{n,1/2}$ are the Whittaker functions. The wave function of the system is identical, apart from a constant, with the Coulomb Green function:

$$\Psi_f(\mathbf{r}, \mathbf{R})=C(R)G^c(\mathbf{r}, \mathbf{R}). \tag{4}$$

Here, the wave function $\Psi_f$ is normalized to unity:

$$\int|\Psi_f|^2\,d\mathbf{r}=1. \tag{5}$$

The dipole moment of the transition is

$$\mathbf{d}_{if}=\int d\mathbf{r}\,\Psi_i^*\mathbf{r}\Psi_f. \tag{6}$$

Instead of $\Psi_i$, we have to substitute Eq. (2). In the calculation of the dipole moment of the transition we can represent the Coulomb Green function in the form

$$G^c(\mathbf{r},\mathbf{R})=\frac{1}{\gamma rR}\sum_l f_{1l}{}^c(r_>)f_{2l}{}^c(r_<)\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\theta,\varphi); \tag{7}$$

here, $\gamma = n^{-1} = (-2E)^{1/2}$,

$$f_{1l}{}^c=(2\gamma)^{-1/\gamma+l+1}r_>^{l+1}\exp(-\gamma r_>)$$
$$\times U\left(-\frac{1}{\gamma}+l+1,\,2l+2,\,2\gamma r_>\right), \tag{8}$$

$$f_{2l}{}^c=\frac{(2\gamma)^{1/\gamma+l+1}\Gamma(-1/\gamma+l+1)}{\Gamma(2l+2)}r_<^{l+1}$$
$$\times\exp(-\gamma r_<)M\left(-\frac{1}{\gamma}+l+1,2l+2,2\gamma r_<\right), \tag{9}$$

$r_\langle$ ($r_\rangle$) is the smallest (largest) of **r** and **R**; $\mathbf{U}(a, b, z)$ and $\mathbf{M}(a, b, z)$ are confluent hypergeometric functions.

Substituting in Eq. (6) the expressions (4) and (7)–(9), we find the dipole moment of the transition. In calculating the integral in Eq. (6) we shall allow for the fact that the selection rules leave only one term with $l = 1$ in the sum over $l$ in Eq. (7). The wave function of the ground state $\Psi_i$ decays rapidly on increase in the distance $r$, so that the radial integral is dominated by the region $r < R$ and we can assume in Eq. (7) that $r_\langle = r$ and $r_\rangle = R$. We then obtain

$$|\mathbf{d}_{if}|^2=\frac{2^{10}C^2\gamma^6(1-\gamma)^{2/\gamma-6}}{\pi(1+\gamma)^{2/\gamma+6}}$$
$$\times R^2\exp(-2\gamma R)\Gamma^2(2-n)U^2(2-n,4,2\gamma R); \tag{10}$$

at large distances, replacing $U(2-n, 4, 2\gamma R)$ with its asymptote $(2\gamma R)^{n-2}$, we obtain

$$|\mathbf{d}_{if}|^2\to\frac{2^{2/\gamma+6}C^2\gamma^{2/\gamma+2}(1-\gamma)^{2/\gamma-6}}{\pi(1+\gamma)^{2/\gamma+6}}R^{2/\gamma-2}\exp(-2\gamma R)\Gamma^2(2-n). \tag{10a}$$

The normalization factor $C$ is found by calculating the integral

$$C^{-2}(R)=\int d\mathbf{r}[G(\mathbf{r},\mathbf{R})]^2. \tag{11}$$

The normalization integral can be calculated using the circumstance that the Green function satisfies everywhere, except at the point $\mathbf{r} = \mathbf{R}$, the Schrödinger equation

$$\Delta G^c+2\left(\frac{1}{r}+E\right)G^c=0. \tag{12}$$

Writing down the equation derived from Eq. (12) by differentiation with respect to the energy

$$\Delta\frac{\partial G^c}{\partial E}+2\frac{\partial G^c}{\partial E}\left(\frac{1}{r}+E\right)=-2G^c, \tag{13}$$

multiplying Eq. (12) by $\partial G^c/\partial E$ and Eq. (13) by $G^c$, subtracting the latter from the former, and integrating, we finally obtain

$$\int d\mathbf{r}\left(\frac{\partial G^c}{\partial E}\Delta G^c-G^c\Delta\frac{\partial G^c}{\partial E}\right)=2\int d\mathbf{r}(G^c)^2. \tag{14}$$

Applying the Green theorem to Eq. (14), we can go over from the integral over all space (with the exception of the point $\mathbf{r} = \mathbf{R}$) to the integral over a spherical surface centered at the point $\mathbf{r} = \mathbf{R}$ and characterized by an infinitesimally small radius $\rho$. Integrating with respect to the angle $\varphi$ (the integrand is independent of this angle because of the axial symmetry of the problem) and going over from the derivative with respect to $E$ to the derivative with respect to $n$, we obtain

$$\int d\mathbf{r}(G^c)^2 = \pi n^3 \lim_{\rho\to 0} \rho^2 \int_0^\pi d\vartheta \sin\vartheta \left( G^c \frac{\partial^2 G^c}{\partial n\, \partial \rho} - \frac{\partial G^c}{\partial n}\frac{\partial G^c}{\partial \rho} \right), \tag{15}$$

where $\boldsymbol{\rho} = \mathbf{r} - \mathbf{R}$ and $\vartheta$ is the angle between the vectors $\boldsymbol{\rho}$ and $\mathbf{R}$. We shall now substitute in Eq. (15) the Coulomb Green function in its closed form[30]

$$G^c(\mathbf{r}, \mathbf{R}) = \frac{\Gamma(1-n)}{2\pi\rho}\left[M'_{n,1/2}(\eta)\, W_{n,1/2}(\xi) - M_{n,1/2}(\eta)\, W'_{n,1/2}(\xi)\right],$$
$$\xi = \frac{r+R+\rho}{n}, \quad \eta = \frac{r+R-\rho}{n}. \tag{16}$$

The part of Eq. (15) in the parentheses is proportional to $\rho^{-2}$. Since it is independent of the angle $\vartheta$ at $\rho = 0$, we can easily integrate Eq. (15) and go to the limit $\rho = 0$. The result is then

$$\int (G^c)^2 d\mathbf{r} = \frac{n^3}{2\pi}\frac{\partial}{\partial n}\Phi(n, R). \tag{17}$$

If we express the coefficient $C = (\int (G)^2 d\mathbf{r})^{-1/2}$ in accordance with Eq. (17) and substitute the resultant expression into Eq. (10), we obtain the following final expression for the dipole moment of the transition:

$$|\mathbf{d}_{if}|^2 = \frac{2^{11}\gamma^9 (1-\gamma)^{2/\gamma-6}}{(1+\gamma)^{2/\gamma+6}} R^2 \exp(-2\gamma R)\, U^2(2-1/\gamma, 4, 2\gamma R)$$
$$\times \Gamma^2(2-n)\left[\frac{\partial}{\partial n}\Phi(n, R)\right]^{-1}, \tag{18}$$

$$|\mathbf{d}_{i_f}|^2 \xrightarrow[\gamma R\to\infty]{} \frac{2^{2/\gamma+7}\gamma^{2/\gamma+5}(1-\gamma)^{2/\gamma-6}}{(1+\gamma)^{2/\gamma+6}} R^{2/\gamma-2}$$
$$\times \exp(-2\gamma R)\, \Gamma^2(2-n)\left[\frac{\partial}{\partial n}\Phi(n, R)\right]^{-1}, \tag{18a}$$

where $\Phi(n, R)$ is given by Eq. (3).

An asymptotic expression for the special case, considered earlier,[19] of the dipole moment of a transition to an ionic state can readily be obtained from Eq. (18a). We can do this by utilizing the expression

$$\Phi(n, R) = 2\pi \lim_{\rho\to 0} \frac{\partial \rho G^c(\mathbf{r}, \mathbf{R})}{\partial \rho}. \tag{19}$$

In the case of the ionic term we can use also the semiclassical expression for the Green function:

$$G(\mathbf{r}, \mathbf{R}) = \frac{1}{2\pi}\frac{\exp(-\gamma_0 \rho)}{\rho}, \tag{20}$$

where $\gamma_0 = (-2EA)^{1/2}$. Substituting Eq. (20) into Eq. (19), we obtain $\Phi(n,R) = -\gamma_0$. Bearing in mind that $dn_0/dn = (n_0/n)^3$ and $n_0 = 1/\gamma_0$, we find that

$$\frac{\partial \Phi(n, R)}{\partial n} = \frac{\gamma^3}{\gamma_0}, \tag{21}$$

which leads to Eq. (25) of Ref. 19 that, in the $s$-scattering case, differs only by a factor $B$ which is unimportant in our problem; this factor represents a correction for the finite nature of the radius of the interaction of an electron with a neutral particle Y. The coefficient $C$ in front of the ionic term is given by $C^2 = 2\pi\gamma_0$.

Equation (18) represents the solution of the second of the problems in the electron part of the task, which is the calculation of the dipole moment of the transition. We may find that the final expression for the dipole moment of the transition should include explicitly $(\partial\Phi(n,R)/\partial n)^{-1}$. However, we shall show later that this is not essential because this quantity is cancelled out in the final expression for the reduced absorption coefficient [see Eq. (25)].

We shall now consider calculation of the slope of the term $\Delta F = |dE/dR|$. Naturally, we can find $|dE/dR|$ by differentiating numerically the $E(R)$ dependence obtained by solving the transcendental equation (3). However, there is a more elegant way of solving this problem. In order to find $dE/dR$, we shall supplement the function $\Phi(n, R)$ at a point satisfying Eq. (3) by increments $dn$ and $dR$ such that Eq. (3) is retained with the same value of $a_0$ as before, and the increment

$$d\Phi = \frac{\partial \Phi}{\partial n} dn + \frac{\partial \Phi}{\partial R} dR$$

vanishes, which gives the following expression for $dE/dR = (dn/dR)(1/n^3)$:

$$\frac{dE}{dR} = -\frac{1}{n^3}\frac{\partial\Phi/\partial R}{\partial\Phi/\partial n}. \tag{22}$$

After simple transformations and direct differentiation of Eq. (3), we find that

$$\frac{d\Phi}{\partial R} = -\frac{n\Gamma(1-n)}{R^2} M_{n,1/2}(2\gamma R)\, W_{n,1/2}(2\gamma R), \tag{23}$$

$$\frac{dE}{dR} = \frac{\Gamma(1-n)}{n^2 R^2} M_{n,1/2}(2\gamma R)\, W_{n,1/2}(2\gamma R)\left(\frac{\partial}{\partial n}\Phi(n, R)\right)^{-1}. \tag{24}$$

In calculation of $dE/dR$ we can use Eq. (24). However, it should be noted that the quantity $(\partial\Phi(n,R)/\partial n)^{-1}$ is contained both in $|\mathbf{d}_{if}|^2$ of Eq. (18) and in $\Delta F = |dE/dR|$ of Eq. (24). This allows us to derive a simple analytic expression for $q$ if we substitute Eqs. (18) and (24) into Eq. (1). Ignoring $U_i$ within the angular brackets in Eq. (1), we obtain

$$q = \frac{2^{15}\pi^3\omega}{3c}\sum_\omega \frac{(1-\gamma)^{2/\gamma-5}(\gamma R_\omega)^6 \exp(-2\gamma R_\omega)}{(1+\gamma)^{2/\gamma+6}}$$
$$\times U^2(2-n, 4, 2\gamma R)\left|\frac{\Gamma(1-n)}{M_{n,1/2}(2\gamma R_\omega)\, W_{n,1/2}(2\gamma R_\omega)}\right|. \tag{25}$$

Equation (25) together with the equation for the terms (3) allows us to find the absorption spectrum of a collisional H + Y complex using the zero-radius potential approximation.

In the case of asymptotically large values of $R$, we have $M_{n,1/2}(2\gamma R)\cdot W_{n,1/2}(2\gamma R) \to \Gamma^{-1}(1-n)$, which leads to

$$q \to \frac{2^{11}\pi^3\omega}{3c}\sum_\omega \frac{2^{2/\gamma}\gamma^{2/\gamma+3}(1-\gamma)^{2/\gamma-2}R_\omega^{2/\gamma+2}\exp(-2\gamma R_\omega)}{(1+\gamma)^{2/\gamma+6}}$$
$$\times \Gamma^2(2-n). \tag{26}$$

However, we should point out that the asymptote given by Eq. (26) is correct only at very large distances between the colliding particles and sufficiently far from atomic lines, which reduces the range of its validity to the asymptote of the ionic term $1/R \ll |EA|$. When the line of an atomic transition is approached, the reduced absorption coefficient rises in accordance with $q \propto (\Delta E_n)^{-2}$, where $\Delta E_n$ is the offset from the frequency (energy) of the atomic line. Equation (25) is valid in the quasistatic range where $\Delta E_n \gg \Omega_W$: $\Omega_W$ is the Weisskopf frequency known from the theory of broadening of spectral lines. The range $\Delta E_n \lesssim \Omega_W$ is narrow and, therefore, it cannot be seen on the scale shown in Fig. 1.

The expressions for the reduced absorption coefficient are obtained above in terms of atomic units and they have the dimensions of length to the fifth degree. In order to go over to the dimensions [cm$^5$], usually employed in the experiments, the results of the calculations based on Eq. (25) should be multiplied by $(0.529 \cdot 10^{-8})^5 = 4.14 \cdot 10^{-42}$.

## 3. RESULTS OF CALCULATIONS

Figures 1–3 give the results of calculations carried out for different values of the scattering length $a_0$. In all these figures the upper part shows the electron terms and the lower part is the spectrum, i.e., the dependence of the reduced absorption coefficient $q$ on the energy $E = U_f$ of the state in which the transition terminates. The spectra and the terms are shown for the sake of convenience in the same figure; such a representation helps us to understand more easily which range of distances contributes to a transition at a given energy. If the scattering length is $a_0 = 2.61$, which corresponds to the presence of a stable negative ion Y$^-$ with an electron affinity of 2 eV $[EA = -(2a_0^2)^{-1}]$ the term is nearly ionic. If $n < 2$, there is no second term at all and the absorption spectrum can be interpreted as a transition from a lower covalent state to an upper ionic state. In this case the results of a calculation of the spectrum are in agreement with the results of calculations performed in the ionic model approximation; the discrepancy does not exceed 25% and the separation from the atomic line greater than the region of the interaction of the covalent excited term with the ionic term. If $n > 2$ the ionic term exists again, but in this case one value of the energy may correspond to two or more values of $R$.

Figure 1 shows the contributions made to the spectrum both by the ionic and repulsive branches. It follows from Fig. 1 that the contribution of the repulsive part of the term is considerably greater and this is due to the much higher values of the dipole moment of the transition. Reduction in the electron affinity energy of Y (i.e., an increase in $a_0$) makes the contribution to the intensity of the spectrum made by the transition to the ionic part of the term comparable with the contribution of the repulsive branch (Fig. 2). However, the

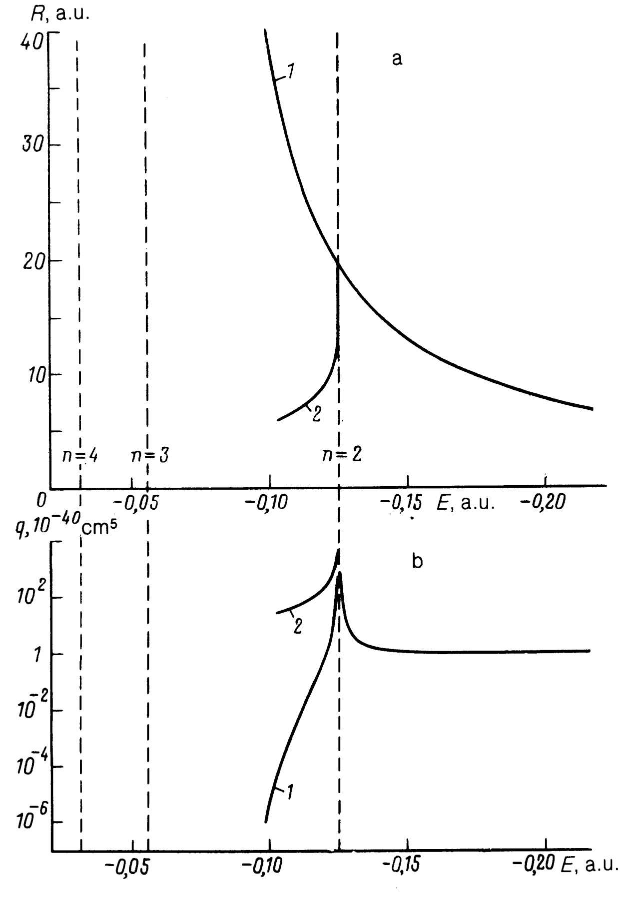

FIG. 1. a) Electron terms of HY; b) contributions made to the reduced absorption coefficient by various parts of the term, considered as a function of the energy of the excited state and calculated using Eq. (25). The vertical dashed lines at $n = 1, 2, 3$, and 4 correspond to the energy levels of the hydrogen atoms. The same numbers are used in the upper and lower parts of the figure to denote the corresponding parts of the term and spectrum; $a_0 = 2.61$.

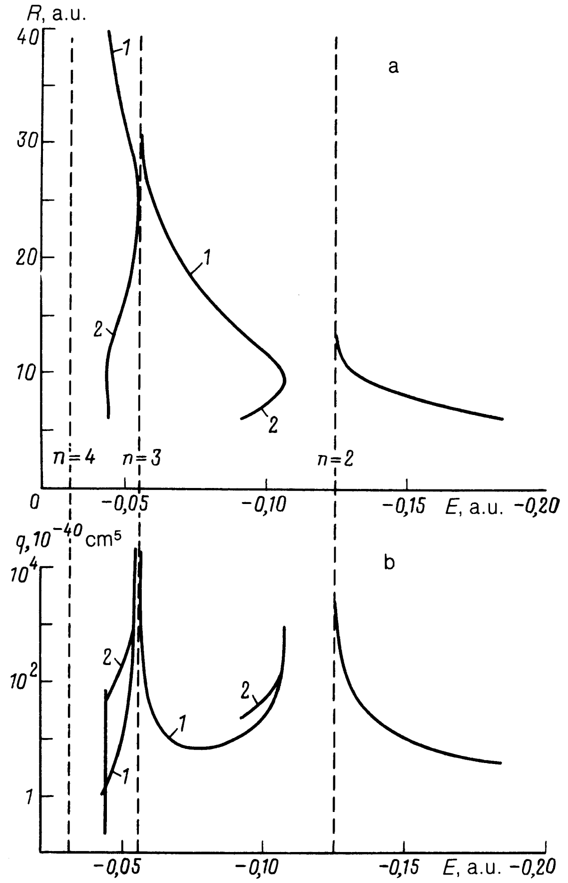

FIG. 2. The same as in Fig. 1, but for $a_0 = 5.22$.

larger the difference between this and the ionic term, the larger the region of interaction of the ionic and covalent terms.

We also carried out calculations that model the spectrum in the case when $EA = 0$ ($|a_0| \to \infty$). In practice, the case $a_0 = 100$ corresponds to $EA = 0$, so that on further increase in $a_0$ there are no changes in the structure of the terms. Reversal of the sign of $a_0$ when the absolute value of this quantity is large (for example, the change from $a_0 = 100$ to $a_0 = -100$) again does not affect the results. Such large absolute values of the scattering length are not encountered in practice (at least in the case of atoms), but already for $|a_0| \gtrsim 10$ the structure of the terms and the spectrum depend weakly on $a_0$.

The spectrum includes contributions not only from the regions of rise near the atomic lines, but also due to singular points in other spectral ranges. These singular points correspond to $\Delta F(R_\omega) = 0$ in Eq. (1) or to $M_{n,1/2}(2\gamma R)\, W_{n,1/2}(2\gamma R) = 0$ in Eq. (25). The regions adjoining these singular points must be considered additionally allowing for the quantum effects in the nuclear motion. More than one extremum may appear for one term and there may be corresponding maxima in the spectrum because of oscillations of the potential curve. In the case of low values of $a_0^{-1}$, even when the distance between the colliding particles is large, the term HY deviates considerably from the atomic term, its orientation is almost parallel to the internuclear axis ($dE/dR$ is always small), and it oscillates slowly approximately near the middle of the energy interval between the $n = 3$ and $n = 4$ lines. When $|a_0|^{-1}$ is increased, the parts of the terms with a central slope are retained, but they lie near the atomic lines, so that it is logical to call them satellites (Fig. 3). The satellites are located in the spectrum on the high or low values of the energy relative to the atomic lines, depending on the sign of $a_0$: for positive values of $a_0$ the offset from the atomic line is positive, whereas for negative values of $a_0$ it is negative.

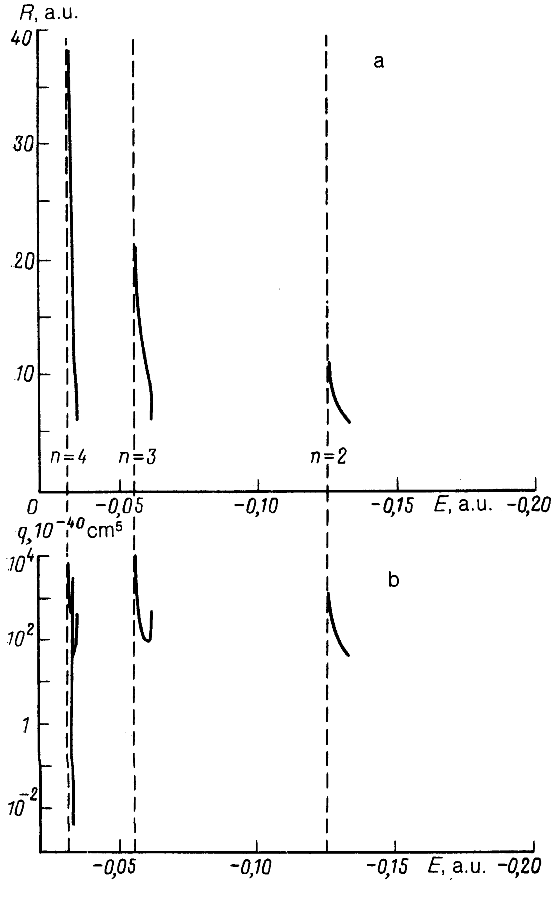

FIG. 3. The same as in Fig. 1, but for $a_0 = -1.2$.

All the spectra in the interval from $n = 3$ to $n = 4$ show steep falls of the intensity when the function $U(2-n, 4, 2\gamma R)$ passes through zero [see Eq. (25)]. This obviously demonstrates that the asymptote $U(2-n, 4, 2\gamma R) \to (2\gamma R)^{n-2}$, which is valid at high values of $\gamma R$, cannot be used and, consequently, the asymptotic expressions (10a), (18a), and (26) are incorrect for this range of parameters. Therefore, the resultant absorption spectrum is obtained by adding the contributions due to transitions to different parts of the term and then the spectrum does not have such steep falls of the intensity to zero: instead there is some reduction in the total absorption coefficient. The calculated values of the reduced absorption coefficient $q$ at the points in the figures where $M_{n,1/2}(2\gamma R)\, W_{n,1/2}(2\gamma R)$ and $U(2-n, 4, 2\gamma R)$ vanish are finite due to the finite nature of the step along $R$ ($\Delta R = 0.5$ a.u.).

## 4. GENERALIZATION OF THE THEORY TO THE CASE OF A MANY-ELECTRON ATOM WITH ONE OUTER ELECTRON

We shall now consider briefly a more complex problem in which the hydrogen atom is replaced by some many-electron atom, but which has only one outer electron. Part of the problem related to the terms of this system has been analyzed earlier[19,27,31] and we shall not consider it here. We shall derive expressions for the dipole moment of a transition and for the spectrum on the assumption that the problem of the terms is solved.

Alkali metal atoms are classical examples of the atoms with just one outer electron but the same description can be applied also to many excited states of other atoms. It is then usual to consider the motion of the outer electron in the effective field of the core $X^+$, which includes not only the Coulomb part, but also a short-range correction $V_x$ which lifts the degeneracy of the spectra $l$ and this should modify greatly also the structure of the spectrum being analyzed. This is formally due to the fact that the Green function can no longer be represented in the form of Eq. (16), where the factor $\Gamma(1-n)$ that has poles for natural values of $n$ corresponds to resonant levels of the hydrogen atom. The Green function with a short-range correction can be represented in the form of Eq. (7), provided we replace the radial Coulomb functions $f_{1l}^c$ and $f_{2l}^c$ with $f_{1l}$ and $f_{2l}$, satisfying the radial Schrödinger equation with the short-range correction $V_x$. The functions $f_{1l}$ and $f_{2l}$ should be described by the following asymptotes when the distances are large:

$$f_{1l}(r) \to r^{1/\gamma} \exp(-\gamma R), \tag{27}$$

$$f_{2l}(r) \to r^{-1/\gamma} \exp(\gamma R), \tag{28}$$

where $f_{2l}$ is regular at zero.

The methods of a quantum defect[32,33] and of a modified orbital quantum number are used most frequently in studies of the problem of supplementing the Coulomb potential with a short-range potential within the semiempirical approach framework. We shall adopt the latter of these two methods proposed by Simons[34] and used successfully on a number of occasions:[35-38]

$$V_x=\sum_l \frac{B_l}{r^2}|lm\rangle\langle lm|, \tag{29}$$

where $B_l$ are constants depending on the individual atom and on the orbital quantum number, and $|\mathrm{lm}\rangle\langle\mathrm{lm}|$ is the operator of projection onto the space of the spherical functions. When this potential is used, the functions $f_{1l}$ and $f_{2l}$ can be obtained from Eqs. (8) and (9) by the substitution of $l\to s_l$, where $s_l=l+\Delta_l$ is the effective orbital quantum number. The positions of the levels of an atom X are then determined by poles of $\Gamma(-n+s_l+1)$ in an expression similar to $f_{2l}$ described in Ref. 9, which reduces the condition that $n-s_l$ is a natural number.

If X is an alkali metal atom in its ground state, the normalized wave function is

$$\Psi_i=\left(\frac{2}{\Delta_0+1}\right)^{\Delta_0+3/2}\Gamma^{-1/2}(2\Delta_0+3)r^{\Delta_0}\exp\left(-\frac{r}{\Delta_0+1}\right)Y_{00}. \tag{30}$$

The defect of the orbital quantum number for the wave with $l=0$ is given by $\Delta_0=n_0-1$, whereas the parameter $n_0$ is related to the ground-state energy $E_a$ of an atom by $n_0=(-2E_a)^{-1/2}$. Proceeding as before in the case of the hydrogen atom, we can obtain an expression for the dipole moment of the transition:

$$|\mathbf{d}_{if}|^2=\left(\frac{2}{\Delta_0+1}\right)^{2\Delta_0+3}\frac{C^2}{\pi}(2\gamma)^{4\Delta_1+6}R^{2\Delta_1+2}\exp(-2\gamma R)$$
$$\times U^2(-n+2+\Delta_1,4+2\Delta_1,2\gamma R)\frac{\Gamma^2(-n+\Delta_1+2)\Gamma^2(5+\Delta_0+\Delta_1)}{\Gamma^2(4+2\Delta_1)\Gamma(2\Delta_0+3)}$$
$$\times\left(\gamma+\frac{1}{\Delta_0+1}\right)^{-2(5+\Delta_0+\Delta_1)}F^2\Bigg(-n+2+\Delta_1,5+\Delta_0+\Delta_1,4+2\Delta_1',2\gamma\Big/$$
$$\left(\gamma+\frac{1}{\Delta_0+1}\right)\Bigg), \tag{31}$$

where $F(a,b,c,z)$ is a hypergeometric function. The expression (31) reduces to Eq. (10) if the defects of the orbital quantum number of the $s$ and $p$ waves were allowed to vanish: $\Delta_0=\Delta_1=0$.

The expression given by Eq. (17) is derived for the normalization integral in the case when the potential is of pure Coulomb type, but it can also be generalized to the Coulomb potential with a short-range correction. We note that, in general, the Green function can be written in the form

$$G(\mathbf{r},\mathbf{R})=\frac{f(\rho,n,R)}{2\pi\rho},\qquad f(0,n,R)=1. \tag{32}$$

Writing down the Schrödinger equation with a short-range correction for the Green function $G(\mathbf{r},\mathbf{R})$ and proceeding exactly as in the derivation of Eq. (17), we obtain

$$\int G^2\,d\mathbf{r}=\frac{n^3}{2\pi}\frac{\partial}{\partial n}f', \tag{33}$$

where $f'=(\partial f/\partial\rho)_{\rho=0}$. In the pure Coulomb potential case we find that $f'$ is identical with the function $\Phi\ (n,R)$ introduced above. In general, $f'$ is given by

$$f'=\Phi(n,R)+\frac{2\pi}{\gamma^2R}\sum_l\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\theta,\varphi)[f_{1l}f_{2l}-f_{1l}{}^cf_{2l}{}^c]. \tag{34}$$

The summation over $l$ in Eq. (34) should be carried out formally from zero to infinity, but in practice it is sufficient to include only the first few terms for which the shift of the levels relative to those of the hydrogen atom is significantly different from zero. The transcendental equation for the terms can be written in the form

$$f'=-a_0{}^{-1}. \tag{35}$$

An analysis of the kind preceding Eq. (22) for the slope of the term of an excited state remains valid also in the more general case, like the expression itself, provided we make the substitution $\Phi(n,R)\to f'(n,R)$.

Generalization of Eq. (22) and of its corollary to that for the potential of the purely Coulomb nature yields

$$\frac{dE}{dR}=-\frac{1}{n^3}\left[\frac{\partial\Phi}{\partial R}+\frac{2\pi}{\gamma}\sum_l\left(\frac{2l+1}{4\pi}\right)^{1/2}\right.$$
$$\left.\times Y_{l0}\frac{\partial}{\partial R}\left(\frac{f_{1l}f_{2l}-f_{1l}{}^cf_{2l}{}^c}{R^2}\right)\right]\left(\frac{\partial f'}{\partial n}\right)^{-1}, \tag{36}$$

where $\partial\Phi/\partial R$ is given by Eq. (23). The final expression for $q$ is obtained by substituting in Eq. (1) the square of the dipole moment from Eq. (31) and also $\Delta F(R_\omega)=|dE/dR|$ in the form of Eq. (36), which gives

$$q=\frac{32\pi^3\omega}{3c}\sum_\omega\left(\frac{2}{\Delta_0+1}\right)^{2\Delta_0+3}(2\gamma)^{4\Delta_1+6}R^{2\Delta_1+4}\exp(-2\gamma R)$$
$$\times\left(\gamma+\frac{1}{\Delta_0+1}\right)^{-2(5+\Delta_0+\Delta_1)}\frac{\Gamma^2(-n+\Delta_1+2)\Gamma^2(5+\Delta_0+\Delta_1)}{\Gamma^2(4+2\Delta_1)\Gamma(2\Delta_0+3)}$$
$$\times U^2(-n+2+\Delta_1,4+2\Delta_1,2\gamma R)$$
$$\times F^2\Bigg(-n+2+\Delta_1,5+\Delta_0+\Delta_1,4+2\Delta_1,2\gamma\Big/$$
$$\left(\gamma+\frac{1}{\Delta_0+1}\right)\Bigg)\left|\frac{\partial f'}{\partial R}\right|^{-1}, \tag{37}$$

where

$$\frac{\partial f'}{\partial R}=-\frac{n\Gamma(1-n)}{R^2}M_{n,1/2}(2\gamma R)W_{n,1/2}(2\gamma R)$$
$$+\frac{2\pi}{\gamma}\sum\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\theta,\varphi)$$
$$\times\frac{\partial}{\partial R}\left[\frac{f_{1l}(R)f_{2l}(R)-f_{1l}{}^c(R)f_{2l}{}^c(R)}{R^2}\right]. \tag{38}$$

The derivative $\partial/\partial R$ in Eq. (38) can easily be obtained analytically employing the familiar expressions for differentiation of the confluent hypergeometric functions.[39] Equation (38) is a generalization of Eq. (25). We can say that in this case once again we can eliminate the derivative with respect to the energy parameter $n$ in the final result.

We shall now list the main limitations of the theory.

1. The electron wavelength near a neutral Y center should be large compared with the characteristic radius of the interaction of the electron with the Y center, $\rho\sim1$ a.u., or

more exactly the following conditions should be obeyed:

$$2\left|E+\frac{1}{R}\right|\ll 1.$$

In those regions where the above relationship is not satisfied sufficiently well the results are simply qualitative.

2. The above theory is inapplicable in the case when an atom of Y has a resonance in its low-energy scattering spectrum. This resonance corresponds to $L\neq 0$, where $L$ is the orbital momentum of an electron.

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(1) The atomic system of units is used here.

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